

Summary Report

Actinide Migration Evaluation (AME) for the Rocky Flats Environmental Technology Site.

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Gregory R. Choppin, David L. Clark, David R. Janecky,

Leonard J. Lane, D. Kirk Nordstrom,

Introduction. The Actinide Migration Evaluation (AME) group was established to provide guidance on issues of actinide behavior and mobility in surface water, groundwater, and soil environments. The AME group draws on the state-of-the-art understanding in the scientific community of actinide chemistry, geochemistry, migration, soil erosion, and sediment and contaminant transport processes. This knowledge is used to help characterize current environmental conditions at RFETS and recommend a path forward for Site personnel for long-term protection of surface water quality during and after Site closure. The AME group has developed a set of urgent, near- and long-term goals that include (i) addressing actinide migration concerns of importance to the Site, (ii) development of an understanding of environmental actinide migration mechanisms in light of recent surface water exceedences, (iii) evaluation of the impacts of actinide migration on remedial actions, (iv) assessing the protectiveness of soil action levels on surface water quality, and (v) assessing actinide migration in terms of long-term surface water compliance at Site closure and potential down-stream impacts.

AME External Advisory Team. The Actinide Migration Evaluation activity at Rocky Flats Environmental Technology Site brings together technical, management and external advisory personnel to facilitate integration and review of RFETS remediation, D&D and monitoring of planning and projects. Where appropriate, the external advisory team identifies research, techniques and approaches that can be used to solve short- and long-term issues. The external advisory team covers a broad range of relevant expertise, and the advisors are explicitly independent of RFETS-funded projects on AME. The present core External Advisory Team includes:



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Dr. David L. Clark; LANL, actinide chemistry and spectroscopy expertise. 1996-present
Dr. David R. Janecky; LANL, actinide & environmental geochemistry expertise. 1996-present
Dr. Gregory R. Choppin; Florida State University, actinide chemistry expertise. 1997-present
Dr. D. Kirk Nordstrom; USGS, hydrogeochemistry expertise. 1997-present
Dr. Leonard J. Lane; USDA, erosion and sediment transport expertise. 1999-present

Other reviewers and advisors are brought to provide specific expertise as necessary, and have included Dr. Sumner Barr (2000, LANL, air transport monitoring and modeling).

Basic Actinide Environmental Behavior. Extensive research has been conducted in the U.S. and internationally on the environmental behavior of actinide elements in a very diverse set of environments over the past 30-40 years. This has provided a rather good base of understanding of the major types of species and their transport mechanisms in soils and natural waters.

In natural waters plutonium solubility is limited by the formation of amorphous $\text{Pu}(\text{OH})_4$ or polycrystalline PuO_2 . A reasonable estimate for the solubility product (K_{sp}) of $\text{Pu}(\text{OH})_4$ is approximately 10^{-54} , which approaches 10^{-64} as the amorphous $\text{Pu}(\text{OH})_4$ ages to crystalline PuO_2 . This estimate puts an upper limit on the amount of dissolved (i.e. ionic/molecular) Pu that can be present, even if higher oxidation states such as Pu(V) or Pu(VI) are the more stable solution forms. Pu(V) has a low tendency to hydrolyze and form complexes with ligands, and is much less likely to be sorbed to solid surfaces and colloidal particles than the other oxidation states of plutonium. While PuO_2 has a solubility range of 10^{-10} - 10^{-13} M, the total observed concentrations above PuO_2 however, are often in the range 10^{-8} - 10^{-9} M, and limited by the formation of the highly insoluble amorphous $\text{Pu}(\text{OH})_4$ on the surface. Moreover, in many natural waters, actual Pu concentrations are often on the order of 10^{-15} M (similar to global fallout) and these low values may be traced to sorption processes. Sorption of hydrolyzed Pu(IV) in natural water on mineral surfaces and surfaces coated with organic material is accountable for the very low observed concentrations of dissolved Pu even in the absence of $\text{Pu}(\text{OH})_4$ (am) or PuO_2 (c). The strong tendency of $\text{Pu}(\text{OH})_4$ to sorb on surfaces is a dominant and often controlling feature in plutonium geochemistry. Due to the very low solubility of Pu(V)/Pu(IV), the primary path of Pu migration is usually migration of colloidal particles to which Pu(IV) is sorbed.

By contrast to plutonium, uranium has less redox activity and is present in natural and sea waters as soluble complexes. In surface waters or waters in soils of carbonaceous material, uranium is present as $\text{UO}_2(\text{CO}_3)_n^{2n-2}$ ($n = 1-3$). Only in reducing waters is uranium(IV) present, and uranium(IV) has an insignificant role in natural waters. Americium exists only in the trivalent state and can be present environmentally, as complexed species (eg. $\text{Am}(\text{OH})_n^{2-n}$, $\text{Am}(\text{CO}_3)^+$, $\text{Am}(\text{OH})(\text{CO}_3)^0$, etc.) and sorbed to colloids. Thus its behavior can resemble that of uranium or plutonium, depending on the pH and the anions present in the water of the particular environment.

AME Results and Findings.

Conceptual Model Development. One of the early activities of the AME process was the development of a Conceptual Model document. This document has several key purposes, and in particular was intended to serve as an integration focus for Site, advisory team and public evaluation. Documentation of the conceptual understanding of potential migration pathways and processes for actinides in the environment at RFETS established a framework for involvement and discussions. Within that framework, the path forward and specific tasks have been defined, prioritized and implemented, with a mechanism for continuous integration of results and refinement of the conceptual model. The AME is now at the point of having a hierarchy of documents extending from the high level Conceptual Model, to the Pathway Analysis, to specific technical reports on project results, integration and reviews.

Environmental Chemistry Issues – Plutonium/Americium. The data amassed during AME studies is consistent with our expectations of plutonium and americium chemical behavior in the environment. The data indicate that plutonium and americium in RFETS surface waters have extremely low concentrations in the femptomolar (10^{-15} M) range, similar to global fallout. Site-specific studies indicate that reducing conditions do not remobilize plutonium, and that the bulk of plutonium and americium is associated with small ($< 2\mu\text{m}$) colloidal particles that will readily settle in ponded water. These results are consistent with the known chemical behavior of plutonium(IV) and americium(III). Extended X-ray Absorption Fine Structure (EXAFS) studies show unambiguously that plutonium in soils taken from the 903 Pad is in oxidation state (IV), in the chemical form (speciation) of insoluble PuO_2 . This is significant in that it had been widely

held at the Site that the chemical form of plutonium was the dioxide, but this had never been proven. The identification of Pu(IV) in the chemical form of PuO₂ is consistent with the observed insolubility of Pu in site-specific waters. Furthermore, the data clearly indicate that physical (particulate) transport is the dominant mechanism for Pu migration at RFETS. This recognition has identified the need for an erosion model, and that for plutonium, soluble transport models based on the K_d approach are inappropriate.

A recent publication in *Science* (2000, 287, 285) on the identification of some amount of a higher oxide in PuO₂(c) does not alter the observed experimental fact that plutonium oxide is very *insoluble* in water, and observation of PuO_x ($x \leq 2.2$) will likely have little or no impact on the nation's approach to radioactive waste management. The solubility of plutonium dioxide is so low that it has always been subject to ambiguities regarding the true identity of the solid and solution phases, and decades of study reveal a range of solubility centered around 10⁻¹¹ M (*Radiochim. Acta* 1999, 86, 101) in water at neutral pH, which is very low indeed. Dozens of measurements, performed all over the world over a period of many decades inherently include the influence of this higher oxide on solubility. If proven to be correct through confirmation by other scientists, this new understanding of plutonium oxide chemistry may provide us with a greatly improved technical understanding that can be used to explain some of the enigmas surrounding plutonium. Nevertheless, plutonium oxides do not dissolve to a significant degree in water!

Similarly, a recent publication in *Nature* (1999, 397, 56) on the observation of colloid-facilitated transport at the Nevada Test Site does not alter our thinking of plutonium migration at RFETS. All the data amassed so far indicates that particulate and colloidal transport is the dominant transport pathway for plutonium in soils at RFETS. The fact that the *Nature* article concludes that any transport model for plutonium migration "must take colloids into account" in fact agrees with our current approach to develop erosion/sediment transport models to predict migration at the Site.

Environmental Chemistry Issues – Uranium. Leakage of liquid wastes from the Solar Ponds has produced a contaminant plume characterized by high concentrations of nitrate and uranium. For the uranium plume, important questions have been raised as to the contribution of naturally occurring uranium relative to waste-derived uranium and as to the processes affecting

uranium mobility such as mineral solubility control. Uranium isotopes (235, 236, and 238) were measured from a few wells to help identify natural vs. anthropogenic sources. Indications of both depleted and enriched uranium with measurable ^{236}U were obtained from the Solar Ponds Plume (SPP) whereas background (uncontaminated) wells were found to have non-detectable ^{236}U and natural activity ratios of $^{235}\text{U}/^{238}\text{U}$. However, as the sampling was limited in scope at the SPP and there is still some possibility of natural uranium contributions in the SPP area. Mixtures of depleted and enriched uranium could occur with little or non-detectable ^{236}U to give the appearance of naturally occurring material. Sampling and isotopic measurements to date have confirmed that uranium isotope systematics can be used to differentiate natural from anthropogenic uranium sources and that both sources exist at RFETS although the extent of natural source material at SPP is unclear. Further measurements are currently underway that should reduce this uncertainty.

A geochemical modeling investigation on the potential for mineral solubility control on uranium mobility has shown that ground waters in the SPP are undersaturated with respect to all U(IV) and U(VI) minerals for which reliable thermodynamic data exist. These results would suggest that uranium should be relatively free to move with the ground water unless attenuated. The fact that the uranium plume as mapped appears distinctly attenuated compared to the nitrate plume suggests four possibilities for attenuation: (1) sorption processes, (2) capillary movement into the vadose zone during dry periods forcing mineral precipitation, (3) uranium precipitated immediately beneath the SPP as leaking solutions reacted with the aquifer material, and (4) a significant fraction was deposited in the pond sludge during evaporation. The tendency for the highest uranium concentrations to be spatially located close to the Solar Ponds (unlike the nitrate) and the tendency for all the ground waters to be undersaturated with respect to uranium mineral solubilities suggests that the third possibility, uranium precipitation in or beneath the SPP and a slow rate of dissolution, is likely. The potential occurrence of elevated uranium in the soils and sediments beneath the SPP needs to be determined because it could have a major influence on the remediation activities for the SPP.

Dissolved species versus particulate transport – scientifically defensible models.

Since all the data amassed indicate that plutonium is present as insoluble plutonium oxides,

transport-modeling calculations (e.g. programs such as RESRAD) that assume soluble forms of plutonium are of no value. The application of RESRAD for risk assessment and plutonium migration is not conservative, as it is not scientifically correct. All data indicate that particulate transport is the dominant migration pathway for plutonium in RFETS soils and surface runoff. As a result, financial and manpower resources have been devoted to the development of scientifically defensible erosion/sediment transport models for plutonium transport at the Site. Indeed, while we point out that plutonium in soils at RFETS is relatively insoluble, uranium on the other hand is prone to formation of soluble compounds. Therefore, uranium will pose a higher probability of aqueous dissolved transport, and dissolved species transport calculations are important for uranium. A thorough understanding of the uranium geochemistry, the uranium source-term, and the overall water balance at the Site are of great importance with respect to uranium transport calculations. For uranium therefore, the application of models such as RESRAD for risk assessment, and the application of more sophisticated geochemical models are both more useful and scientifically defensible.

Public communication. The AME external advisory team has recognized from its inception that communication with public stakeholders is an important responsibility. We are committed to two-way communications about AME approach, documents, reviews, projects, applicable research and concerns. Through this continuous process of public meetings as part of each quarterly meeting of the AME external advisory team, the stakeholders have gained substantial understanding of the complexity of actinide chemistry and environmental behavior. In addition, the external advisory team has gained an essential understanding of the public and regulatory issues involved in applying research concepts and knowledge to remediation and site closure applications. The external advisory team has made a conscious effort to respond to issues and questions raised at public meetings, exemplified by efforts to address questions on plutonium oxide solubility and colloid-facilitated transport. Finally, the external advisory team has worked hard to maintain independence and credibility both with the Site and the concerned public. New members have been added as necessary, with the concurrence of the public, to address changing foci and needs at the Site. This is especially important in dealing with the complicated issues of

actinide (Pu, Am, U) contamination across the broad range of concentrations (greater than 10^{12} from Ci to $< \text{pCi}$), present in contaminated production facilities and soils and sediments.

Path forward. As of June 2000, we propose the following as components to be included in the activities which are important in the plan to achieve closure by 2006:

- Additional technical investigation of pond systems and near term surface water composition should be carried out to have a satisfactory understanding of particulate transport for Pu/Am.
- Based on the understanding gained from the modeling of the solar pond plume, the source term for uranium under the solar ponds is needed.
- Wind erosion and air transport modeling should be continued, particularly for the effects of D&D activities.
- Soil erosion/sediment transport modeling tools should be used to assist in design of future Site configuration conditions at closure.
- Original process waste lines as potential Pu/Am contaminant sources need to be characterized and modeled to improve plans for remedial action.
- Greater focus on the Industrial and Protected Areas, with attention to the connection between D&D and ER/RFCA compliance, should continue.
- Further science studies are needed to assure an adequate understanding of the system to define and justify decisions (IA/PA/RFCA/ER/D&D, etc.).
- Kaiser-Hill and DOE should develop plans to ensure consistency between the concepts and present operations leading to closure and near term site monitoring, and long term stewardship.

Conclusions. The closure activities at RFETS are at an important juncture in the sense that the pressure to meet the 2006 deadline is keenly felt and activities must be clearly focused, efficient, and relevant. Obvious data gaps in information must be identified and the information obtained in the most expeditious manner. Research studies are still necessary but these studies must be kept focused on those issues relevant to safe and appropriate closure of the site. DOE and Kaiser-Hill have done a credible effort of obtaining data for an adequate understanding of site characteristics

and processes to improve the success of site closure. Such efforts must be continued during the final pre-closure period.

As closure approaches and Kaiser-Hill looks forward to completion of its responsibilities it becomes essential to consider the long-term responsibilities of DOE beyond 2006. These long-term considerations, or future stewardship, must be formulated into a plan that fits smoothly with the near-term closure activities. Development of such a plan will be a key ingredient to future land use and to the environmental concerns of the surrounding communities.